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Effect of urea/metal ratio on the performance of NiMoP/Al_2O_3 catalyst for diesel deep HDS

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Abstract Alumina-supported NiMoPOx catalysts have been prepared using urea matrix combustion–decomposition method. The effect of urea/metal ratios on the metal oxide dispersion, the conversion of the metal precursor to oxide and the structure and catalyst performance for diesel HDS has been studied. It is shown that the addition of urea adjusts the metal–support interaction, leading to the easy reduction of the metal oxide over the catalyst surface. It also changes the surface cluster of the oxide and the oxide structure. The addition of urea to metal matrix significantly improves the catalytic diesel HDS performance and increases the catalyst stability. The urea to Ni metal ratio of 2 gives the highest sulfur removal rate in the real diesel HDS process.

Keywords NiMoPOx catalyst · HDS · Diesel · OMX method

Introduction

Increasing stringent environmental regulations and higher energy efficiency requirement have caused new challenges for refinery to deeply remove sulfur from the fuels [1–3]. On the other hand, one of the most remarkable developments in passenger car transport in recent years was the rapid gain of market shares of diesel vehicles—especially in some European countries, due to a better fuel economy (20–30 % of better fuel efficiency) and relative lower fuel price (to some extent due to considerable tax benefits) which led to lower service prices per vehicle km driven of about 30 % for diesel cars comparing to gasoline cars, as well as other well-known characteristics of diesel cars such as reliability and durability, thus the demand for diesel fuel has been continuously increasing in recent years, while the sulfur compounds in diesel fuel are often more refractory than these in gasoline [4–6].

Also with the depletion of the conventional light crude oil reserve, more and lower quality crude oil feedstock is supplied to the refinery, which has to be cracked into fuel fractions using FCC process, causing even more challenge to the HDS process, as the sulfur compounds in the FCC diesel often contains higher content dibenzothiophene (DBT) and dimethyl dibenzothiophene (DMDBT) then the straight run diesel [7–9]. Given an existed refinery, where little space is available for new reactors or devices installation, the only option is to develop a more robust catalyst, which is to be dropped in the existed reactors to achieve the required standards in the diesel. This might be the reason why there are so many works focusing on the novel catalyst development in these years.

Supported NiMo catalyst modified with P has been developed for hydrotreatment of diesel for decades, which is generally prepared using incipient wetness method [10–14], the addition of the PO_4 weakens the interaction of MoS_2 with the alumina support, this giving a high activity, while the nickel helped the direct hydrogenation of the sulfur.

In recent years, urea matrix combustion methods have been developed for hydrotreatment catalyst preparation.

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Sergio [15–17, 19–21] et al. studied the effect of the urea addition on the CoMo, NiMo and CoNiMo catalyst for thiophene HDS reaction, it is found that the urea addition during the preparation stage helped the improved activity is mainly associated with a very efficient interaction between the well-dispersed oxidic precursors on the alumina surface.

It is pointed out that urea combustion step can facilitate well-dispersed Co- and Mo-oxo species (mono and poly-molybdate) formation, whereas the conventional impregnation techniques lead to mixed-metal oxides formation. This was reflected in the sulfurized phase morphology and structural disorder degree of carbon material deposited on the catalyst surface upon the sulfurizing process using thiophene as sulfurizing agent. The preparation method notably affects the thiophene HDS-specific rates, showing the following activity order: UMxD > UMxC > W-CI > WSI > ChM, while an opposite trend for relative rate of HYD to HDS reactions was observed.

Fahai Cao et al. [22–25] prepared series of TiO_2-modified Al_2O_3-supported CoMo catalyst using urea matrix combustion for diesel HDS catalyst preparation, it has been found that catalyst prepared using the urea matrix combustion method had higher pore volume and surface area than those prepared by the co-impregnation and sequential impregnation methods. The UMxC method increased metal loading and avoided formation of inert phase, e.g., β-$CoMoO_4$, for the HDS reaction. TiO_2 promoter made particles on the catalyst surface closer and alleviated the interaction between molybdenum oxide and the support, and facilitated the formation of well-dispersed Co- and Mo-oxo species on catalyst surface, thus resulting in higher HDS catalytic activity than pure γ- Al_2O_3 support without modifiers.

Lai W et al. [25] studied the effect of starch addition on the precursor combustion reaction, properties, active phase, and intrinsic hydrodesulfurization activity of Al_2O_3-supported Ni-Mo catalysts prepared by combustion synthesis in a 1-pot process. The increase in starch addition markedly enhances the molar enthalpy of the combustion reaction, develops the porosity of the catalysts, and improves the reducibility and sulfidability by reducing the interaction of Mo and Ni with the Al_2O_3 support. Thus, the total number of Ni-Mo-S active sites increase, and substantial amounts of the Ni-Mo-S Type II phase forms, increasing the turnover frequency (TOF) for the catalysts. However, excess starch will lead to a large agglomeration of Mo particles, resulting in high MoS_2 stacking and low MoS_2 dispersion.

Based on the above work, we have tried to make Al_2O_3-supported NiMo catalyst by adding urea into $Ni(NO_3)_2$ and ammonium molybdate solution with minimum water added, but the solution gradually generates precipitation during the preparation especially when the solution was kept for a while. To make the solution more stable, we have added phosphoric acid into the urea-Ni-Mo aqueous solution and found that the solution was much more stable with H_3PO_4 addition, Hence, in this work, series of Al_2O_3-supported NiMoPOx was prepared using urea matrix composition method, and the catalysts have been tested for simulated and real diesel HDS. Some interesting results have been obtained.

Experimental

Catalyst preparation

The catalysts were prepared using incipient wetness method. A transparent solution containing 2.96 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ (AHM) (0.99 purity, Alfa Aesar), 1.9 g $Ni(NO_3)_2.6H_2O$ (0.98 purity, AlDrich) and 0.1 g (H_3PO_4 (0.85 purity, AlDrich) and urea was prepared by dissolving the above mixture into 5 ml water, and the solubility of the mixture was adjusted using ammonia water solution. The urea amount to the solution was added according to the urea/Ni mole ratio of 0, 1 and 2. The addition of urea did not change the pH value of the solution. The solution mixture was stable and kept in round bottom flask for further use.

The Al_2O_3 (7.02 g, China Gongquan Chemical, Zibo, surface area, 246 m^2/g) was firstly dried in air at 600 °C for 2 h, then cooled down to room temperature. It is used to impregnate with the above solution according to the pickup volume of the Al_2O_3 support, e.g., 4.9 ml of the above solution. The sample was agitated intermittently at room temperature for 1 h then dried in a carbolite furnace at 200 °C for 4 h.

The estimate composition of the catalyst precursor prepared this way (as metal oxide weight %) is: 6.8 wt % NiO, 18.9 wt %MoO_3 and 0.89 wt % P_2O_5.

The activation and sulfurization

The catalysts were sulfurized using straight run gas oil spiked with dimethyl disulfide (DMDS) (4 wt. % S) as sulfiding agent. The catalyst was dried under N_2 flow (100 mL min^{-1}) for 2 h and then soaked with sulfiding agent and hydrogen flow for 1 h at 150 °C. Subsequently, the liquid-phase sulfidation conditions were set: liquid hour space velocity (LHSV) of 2.4 h^{-1}; H_2/oil volume ratio of 300 N L/L and 30 barg of hydrogen. The temperature was increased at 0.5 °C min^{-1} to 240 °C and kept it for 4 h, then further rising at 0.5 °C.min^{-1} to 340 °C and kept at 340 °C for 2 h. Afterward, the reactor was cooled down to 220 °C under sulfiding agent and H_2 flow condition. After finishing the sulfidation process, the feedstock was switched at 220 °C and the reaction pressure (35 barg),

temperature (340 °C), liquid hour space velocity (1.2 h^{-1}) and H_2/oil volume ratio (250 N L/L) were adjusted to the reaction condition. The temperature was increased up to 340 °C using a heating ramp of 0.5 °C/min.

Catalyst evaluation

The catalysts were tested on parallel at 50 barg, 400 NL/L, 340 °C and liquid hour space velocity (LHSV) of using a model feed and gas oil as feedstocks to compare the feed effect on the catalyst performance. The feed of the model oil is dimethyl dibenzothiophene and quinoline dissolved in decalin solvent, and forming a simulated oil mixture, which composed of sulfur: 6,625 ppm, dimethyl dibenzothiophene and 20,000 ppm dibenzothiophene, nitrogen: 9,210 ppm quinoline. The industrial FCC diesel was provided by a South Asia Refinery, and the properties are shown in Table 1.

The runs were conducted in a trickle bed reactor. The liquid feedstock was continuously fed into the reactor using a Series II high-pressure pump operating in the mode of volumetric flow. A detailed description of the catalytic test procedure is given elsewhere [7]. Briefly, after finishing the sulfidation process, the feedstock was switched at 220 °C and the desirable reaction pressure and temperature (340 °C), liquid hour space velocity (0.6–1.2 h^{-1}) and H_2/oil volume ratio (400 N L/L). Sulfur and nitrogen analysis in the hydrotreated products was carried out on ANTEK 9000VNS instrument as was previously described. The qualitative analysis of sulfur content in the liquid product was carried out using a GC with a sulfur-specific detector (flame-photometric detector).

Catalyst characterization

The catalyst elemental analysis was carried out by INTERTEK using atomic emission spectrometry with inductively coupled argon plasma (ICP) as the excitation source. Carbon and sulfur analysis was carried out by using a Vario EL Elemental analyzer. The samples were digested through oxidative combustion and the gases analyzed with a thermal conductivity detector.

The crystalline phases of the oxidic precursors and the sulfided catalysts were identified by X-ray diffraction (XRD). The specimen were prepared by grinding a small amount of each sample using an agate mortar and pestle and then loaded into a flat sample holder. The data were collected in θ/2θ reflection mode, from 5 to 80° in 2θ.

Temperature-programmed reduction (TPR) analysis of the oxidic precursors was carried out on a Micromeritics AutoChem II 2920 instrument. The samples (110 mg) were pre-treated before analysis with a 25 mL min^{-1} He flow rate, from room temperature up to 150 °C for 30 min. TPR profiles were obtained by using 5 % H_2/Ar and 10 °C.min^{-1} heating rate from room temperature up to 950 °C and held at that temperature for 120 min The textural properties of the catalyst oxide precursor were carried out by physic-sorption at the nitrogen liquid temperature. It was used a Micromeritics ASAP 2020 Surface area and porosity analyzer.

Table 1 The property of the FCC diesel feed for the HDS catalyst test

Fuel properties	FCC feedstock
Sulfur/μg g^{-1}	6,250
Nitrogen/μg g^{-1}	470
Density (15 °C)/Kg m^{-3}	916.8
Boiling point range/ °C	111–382
Total aromatic hydrocarbons/ % mass	41.9
Mono aromatic hydrocarbons/ % mass	21.3
Di-aromatic hydrocarbons/ % mass	19.3
Tri + aromatic hydrocarbons/ % mass	1.4
Cetane index	42.1

Results and discussion

The urea containing metal–organic matrix mixture has been widely studied under air-rich conditions [21, 26–28]. However, it is known that the urea may be combustible with air-rich atmosphere. To avoid the strong exothermic reaction and control the calcinations step, the effect of atmosphere on the thermal treatment process has been studied. Each time, 5.0 gram of the 10 % of urea loaded over Al_2O_3 supports after drying was placed in 9 mm (id) quartz tubes and monitored with a thermal couple placed near the catalyst bed. The reactor was heated in a furnace at 1.5 °C/min under various atmospheres. It is shown that in flowing air, the mixture starts to ignite up at 240 °C and the combustion of urea in air gives a temperature rise from 240 to 275 °C, then cooled down in 20 min, suggesting that the urea combustion occurs in a quick process. In the case of static air system, the ignition of urea stated at 268 °C and the combustion period lasts from 165 min to 180 °C, the temperature rise in the reactor is less than the one in flowing air system.

To study the effect of the inert holding layer effect on the calcinations effect, a catalyst layer without silica carbide on the top is heated in a static air system, and the temperature profile change with the time on stream is almost the same as that with SiC on the top in the static air. This suggests that the silica carbide top layer does not influence on the metal/urea matrix combustion, the main factor influencing the calcination process is the atmospheres.

The temperature changes of the urea/metal matrix with the heating time in static air are shown in Figs. 1, 2. It is interesting to see that the U-M-0 sample has a broad period of temperature change, the temperature rise started at 240 °C and increased to 257 °C at 145 min, and the exothermicity gradually disappears until 150 min. The exothermicity of the sample without urea is the decomposition of the nickel nitrate, which takes place at high temperature, but is exothermic reaction.

For the sample with urea/min ratio of 1, e.g., U-M-1 sample, the nickel nitrate precursor does not decompose, but a sharp temperature increase occurs at 156 min, and the temperature rose to 285 °C, and then quickly back to the furnace temperature at 162 min. The strong exothermal might result from the reduction of $Ni(NO_3)_2$ by urea. When the U/M ratio is 0.5, or 2, the exothermic reaction started at 270 °C, and finished in a narrow periods. The increase of urea to metal ratio to 2 did not change the reaction starting temperature, but did increase the exothermicity, which can be explained by the nitrate reaction with the urea.

The above results did show that the urea/metal ratio significantly effect on the metal compounds transformation process during the combustion. The atmosphere of the calcinations process changes the chemical reaction process in the catalyst preparation step.

The laser Raman spectra of the NiMoP/Al_2O_3 catalysts prepared using different urea/Ni ratios are shown in Figs. 3, 4. For the alumina-supported NiMoP catalyst without urea added in the preparation stage (urea/metal = 0), three Raman resonance bands have been observed, at 953, 870 cm^{-1} which are ascribed to the Mo = O stretch vibration of $[MoO_4]^{2-}$ and $[Mo_7O_{24}]^{6-}$ clusters. The Raman band at 364 cm^{-1} is due to the asymmetric bending of the Mo–O-Mo bond in the $[Mo_7O_{24}]^{6-}$.

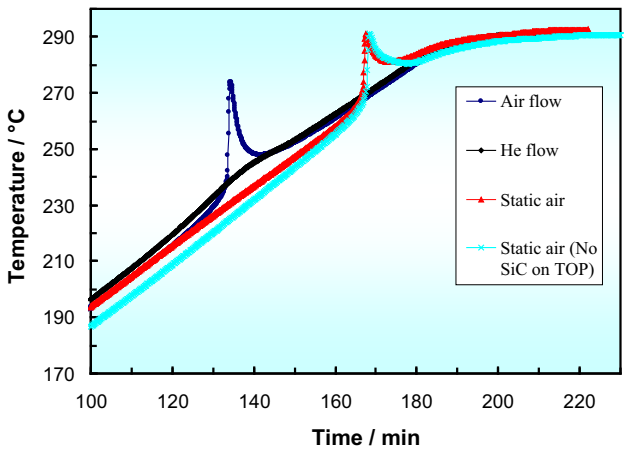

Fig. 1 Atmosphere effect on the temperature change of the catalyst bed during calcination

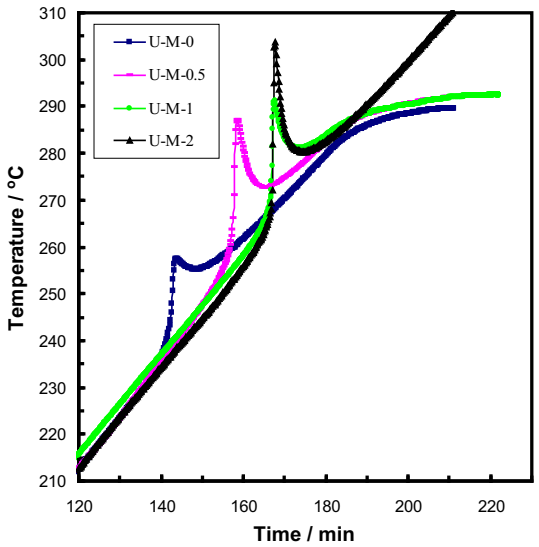

Fig. 2 Effect of Urea/Ni mole ratios on the catalyst bed during calcination

The pronounced shoulder at 870 cm^{-1} indicates that quite a lot of $[MoO_4]^{2-}$ are present over the Al_2O_3 support catalyst, which may easily form $Al_2(MoO_4)_3$, leading to more inert phase of MoO_3 over the catalyst. When urea was added at urea/metal = 1 during the preparation stage, there are still three main Raman bands, while those at 953 and 362 cm^{-1} almost unchanged, while the band intensity at 870 cm^{-1} decrease to some extent. When the urea/metal ratio is increased to 2 in the preparation, the shoulder band at 870 cm^{-1} decreases further. This suggests that adding urea to the catalyst during the preparation helps the formation of bigger molybdenum clusters, which may have less interaction with the support and could be easily

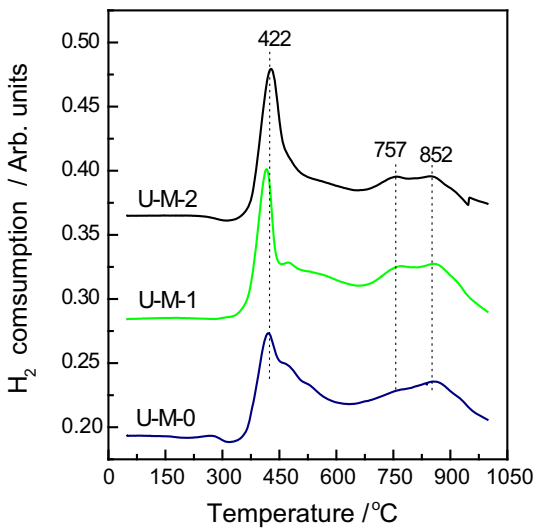

Fig. 3 TPR profiles of the NiMoP catalyst prepare d with different Urea/Ni ratios

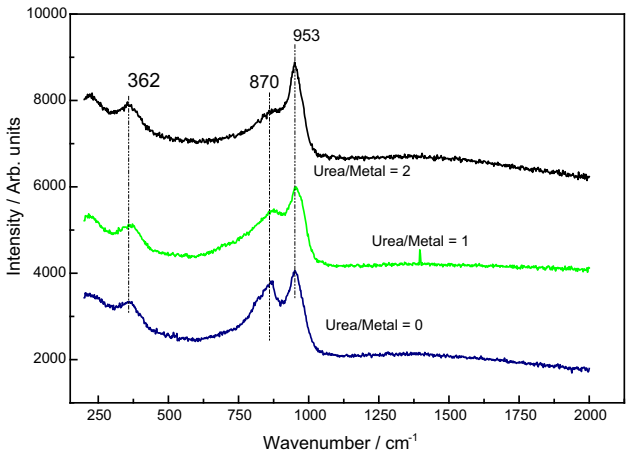

Fig. 4 Laser Raman spectra of the NiMoP/Al_2O_3 catalyst prepared with different Urea/metal ratios

sulfurized, forming the active phase. The reason for the bigger $[Mo_7O_{24}]^{6-}$ clusters may be due to the ligand effect of urea which can depress the formation of MoO_4 ions and also can relieve the support to contact with the MoO_4 ions.

A schematic graph of the MoO_3 cluster presenting over the alumina support is shown in Fig. 5, based on the laser Raman measurement. With the increase urea to metal ratios, the domain size of MoOx increases, thus fewer Mo oxide clusters are directly bond onto Al_2O_3 support. This may be of help for the catalyst activity, as it has shown that $Al_2(MoO_4)_3$ is inert phase for the HDS reaction [21, 26, 29].

The X-Ray diffraction patterns of the NiMoPOx/Al_2O_3 catalyst prepared using different urea/metal ratios are given in Fig. 6. Very broad diffraction peaks at 45, 65 are due to the alumina support. No sharp MoO_3 or NiO phase is detected, suggesting that the molybdenum oxide and Nickel oxide are highly dispersed over the support. However, comparing the diffraction peak at 26.5, which is not seen in the catalyst prepared with urea/metal ratio of 2, but is present in the catalysts with urea/metal = 0 and 1. The

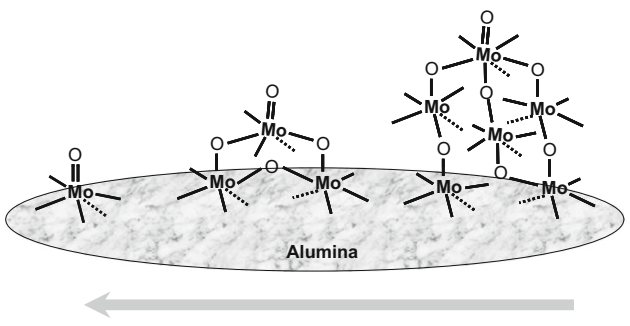

Fig. 5 The schematic graph of the MoOx domain over the Al_2O_3 support prepare using different urea/metal ratio

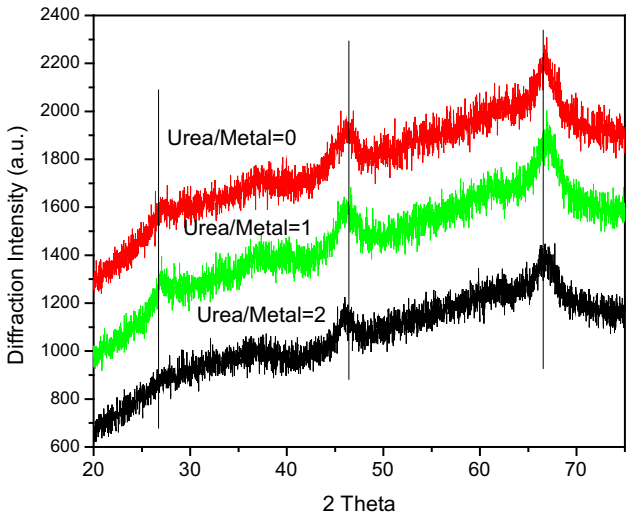

Fig. 6 XRD patterns of the NiMoP/Al_2O_3 catalyst prepared with different urea/metal ratios

peak is tentatively designated to the $NiMoO_4$, which might be formed during the catalyst preparation. Adding more urea in the catalyst preparation can reduce the formation of $NiMoO_4$.

The images of the Al_2O_3-supported NiMoP catalyst prepared using different urea/metal ratios are shown in Fig. 7. It is seen that the catalyst prepared without urea has a relatively smooth surface less uneven surface. When urea/metal of 1.0 is used, the resultant catalyst surface becomes rougher with more bumps and hollow. The surface of the alumina-supported NiMoP prepared using urea/metal = 2 has even more pores and hollows, the surface seems to be more porous and rougher, which may be due to the gas induced pore formation during the preparation, as more urea added to the catalyst will generate more gas and evolved from the catalyst surface,

Catalyst test results

The prepared catalyst has been sulfurized and tested for the HDS performance using model feed as well as the real FCC diesel. The model feed composed of DBT, DMDMT as well as quinoline. The initial tests were carried out at LHSV of 1.2 and 2.4 h^{-1} and temperature of 350 °C, which showed that most sulfur and nitrogen can be completely removed, showing almost no difference among the catalyst performances.

When decreasing the reaction temperature to 340 °C and increasing the LHSV to 4.8 h^{-1}, there are some differences among the catalyst performances. The NiMoP/Al_2O_3 prepared using urea/metal of 1 can reduce sulfur from 26,000 ppm down to 1,277 ppm, and nitrogen from 9,210

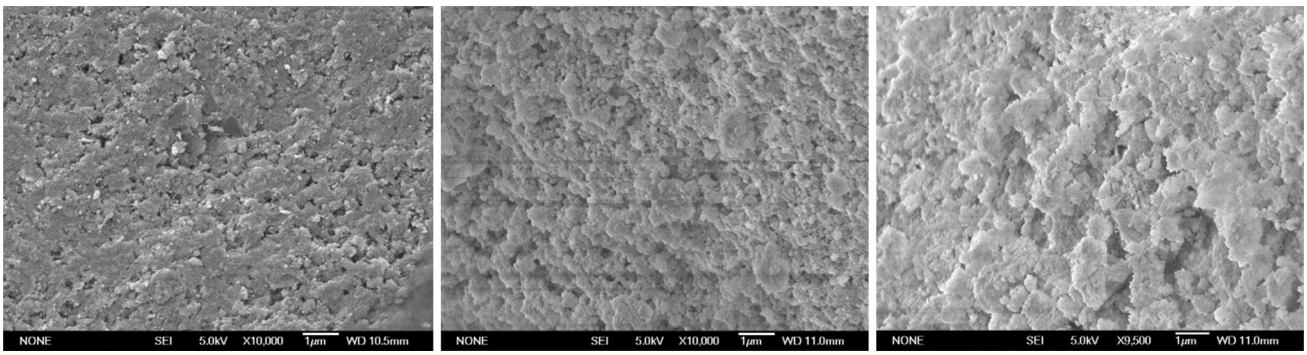

Fig. 7 SEM images of the NiMoP/Al_2O_3 catalysts prepared using different Urea/Ni ratios

to 963 ppm. When urea is added to the catalyst preparation, the sulfur in the oil after HDS decrease to 1,091 and 1,089 ppm, while nitrogen decreases to 895 and 901 ppm, which showed that the addition of urea to the catalyst preparation and them combustion did help to improve the catalyst performance, but increasing the urea/metal ratio to 2.0 is not as good as that with 1.0.

However, when the real industrial FCC diesel feed is used for the catalyst test, the results are shown in Tables 2, 3. Sulfur was reduced from 6,250 ppm to 69 over the NiMoP prepared without urea, and nitrogen was reduced from 470 ppm to 11 ppm, also the cetane number increased to 58 from 42, and the total aromatic content decreases to 23.1 from 41.9 %. The mass balance over this catalyst is about 89 %.

Over the NiMoP/Al_2O_3 catalysts with urea/metal of 1, the sulfur content decreases to 52 ppm and the nitrogen to 5 ppm from 470. The mass balance improves to 91 %, and the resultant diesel cetane number increases to 60, suggesting that the addition of urea for the catalyst preparation using combustion method helps to improve the catalyst HDS performance and increase the cetane number. A further increase of urea/metal to 2 in the catalyst preparation improves the catalyst HDS performance. The sulfur decreases significantly to 29 ppm, while nitrogen almost unchanged to 6 ppm. The total aromatic content decreases slightly to 21.1 % with the liquid recovery ratio further increase to 93 %. These results showed that the addition of urea to the catalyst preparation improve the performance for the real feed, which may be due to the less interaction of the Mo active phase with the support, more Mo7 clusters over the catalyst and also the more porous surface of the catalyst which may provide more sites and routes for the diesel hydrocarbons to diffuse and contact the active phase.

For the simulated feeds test results, the less difference among the three catalysts may be due to that the main hydrocarbon in the feed is decalin, which is smaller than the real feed and easy to diffuse even with less porous catalyst, also the sulfur and nitrogen species are much fewer than the real feedstock. Therefore, the simulated feed test results may not be able to reflect the catalyst performance in the real catalyst performances.

Table 2 The catalyst test results using model compounds

Catalyst	Sulfur in feed	Nitrogen in feed	Sulfur in the product	Remaining nitrogen in product
Urea/metal = 0			1,277	963
Urea/metal = 1	6,625 ppm DMDBT		1,091	895
Urea/metal = 2	20,000 ppm DBT	9,210 quinoline	1,089	901

The catalyst test conditions: PH_2: 35 bar, LHSV: 4.8 h-1, H_2/Oil N/N ratio; 400,Temperature; 340 °C

Table 3 The sulfur and nitrogen content in the diesel products after HDS

Catalyst	Residue S in fuel ppm	Residue N in the fuel ppm	Liquid mass balance	Cetane number	Total aromatics
U-M-0 (260 °C)	69	11	89	58	23.2
U-M-1 (260 °C)	52	5	91	60	22.3
U-M-2 (260 °C)	29	6	93	60.5	21.1

The test conditions: reaction temperature: 340 °C, H_2/oil volume ratio: 400, H_2 pressure: 5.0 MPa. Diesel fuel LHSV: 1.0

Conclusion

Al_2O_3-supported NiMoPOx catalyst has been prepared using urea matrix decomposition–combustion method. The calcination atmosphere and the urea/metal ratios have

significant effect on the thermal chemistry of the catalyst system. To decrease the explosion and get a more stable reproducible catalyst, a static air atmosphere was chosen in this work, so the urea removal process is through combustion of static air and the decomposition of urea. Adding phosphate to the catalyst precursor helps to stabilize the liquid mixture.

The introduction of urea to the catalyst preparation helps to adjust the nickel and molybdenum interaction with the support, addition of urea can help the reduction of the metal and leads to less inert phase like $Al_2(MoO_4)_3$ and $NiMoO_4$ formation. The urea addition also changes the MoO_3 cluster distribution over the alumina support and leads to more porous and rough surface of the NiMoPOx over the catalyst support.

The simulated feed and the real diesel feeds give different HDS performance over the resultant catalyst, due to the complexity of the real feed. The urea/metal ratio has more significant effect on the catalyst performance in the real diesel feed test system.

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